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In re Application of Takuo HIBI, et al

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For : PROCESS FOR PRODUCING CHLORINE

DECLARATION UNDER 37 C.F.R. § 1.132

Honorable Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

I, Kohei SEKI, a Japanese citizen residing at 2-14-13-402  
Imai, Chuo-ku, Chiba-shi, Chiba, Japan, declare:

That I graduated from Hokkaido university, Graduate School of  
Environmental Earth Science, Division of Material Science, master  
degree, in March 1997 and entered Sumitomo Chemical Company Limited  
in April, 1997, in which company I have since then been engaged in  
development of solid catalysts, especially oxidation catalyst;

That I am familiar with the prosecution history of the  
identified-application;

That I am one of the inventors of the identified-application;  
That the following experiment was conducted by me or under my direct  
supervision.

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### Preparation of Samples

#### Sample A

A catalyst was prepared by the following process. That is, 30 g of a titanium oxide powder (STR-60N, 100% rutile crystal, manufactured by Sakai Chemical Industry Co., Ltd.) was kneaded with 20.1 g of pure water and 3.95 g of a titanium oxide sol (CSB,  $\text{TiO}_2$  content: 38% by weight, manufactured by Sakai Chemical Industry Co., Ltd.). At room temperature, a dry air was blown to the kneaded one, which was then dried until suitable viscosity was obtained. After drying, the mixture was sufficiently kneaded again. This kneaded one was extruded into a form of a noodle of 1.5 mm  $\phi$  in size. After drying under air at 60°C for 4 hours, 27.4 g of a white noodle-shaped titanium oxide was obtained. After heating under air from room temperature to 500°C over 1.4 hours, calcination was conducted at the same temperature for 3 hours. After the completion of the calcination, 26.9 g of a white extruded titanium oxide was obtained by cutting the noodle-shaped solid into pieces of about 5 mm in size. Then, 20.4 g of the resulting carrier was impregnated with an aqueous solution prepared by dissolving 0.81 g of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , Ru content: 37.3% by weight) in 8.31 g of pure water, and dried at 60 °C for 2 hours. Then, the resulting solid was dipped in a solution of 4.2 g of a 2N potassium hydroxide solution, 60 g of pure water and 1.02 g of hydrazine monohydrate under nitrogen at room temperature, followed by dipping for 1 hour with stirring every 15 minutes after the reduction, filtration was conducted by using a glass filter. Bubbling occurred on dipping. 500 ml of pure water was added, followed by washing for 30 minutes and further separation by filtration. This operation was repeated five times. The pH of the wash was 9.3 at the first time, and the pH of the wash was 7.3 at the fifth time. To the resulting extruded solid separated by filtration, 50 g of a 0.5 mol/l of potassium chloride solution was added and, after stirring and allowing to stand 30 minutes, the resulting extruded solid was separated by filtration again. This operation was repeated three times. The resulting extruded solid was dried at 60°C for 4 hours to obtain a gray solid. After heating from room temperature to 350°C under air over 1 hour, the solid was calcined



at the same temperature for 3 hours. After the completion of the calcination, 500 ml of pure water was added and the mixture was stirred and, furthermore, the solid was separated by filtration. This operation was repeated five times over 5 hours and, after adding dropwise an aqueous silver nitrate solution to the wash, it was confirmed that potassium chloride is not remained. Then, 20.4 g of a bluish gray extruded ruthenium oxide catalyst supported on titanium oxide was obtained by drying this resultant extruded solid at 60°C for 4 hours.

Incidentally, the calculated value of the content of ruthenium oxide of the catalyst was as follows.

$$\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2(\text{rutil crystal}) + \text{TiO}_2(\text{binder})) \times 100 = 1.9\% \text{ by weight}$$

The calculated value of the content of ruthenium was as follows.

$$\text{Ru} / (\text{RuO}_2 + \text{TiO}_2(\text{rutil crystal}) + \text{TiO}_2(\text{binder})) \times 100 = 1.5\% \text{ by weight}$$

The ruthenium oxide catalyst supported on titanium oxide (2.5 g) thus obtained was diluted by mixing with 10 g of a commercially available spherical (2 mm in size) alumina carrier (SSA995, manufactured by Nikkato Co.) and then charged in a quartz reaction tube (inner diameter: 12 mm). A hydrogen chloride gas (192 ml/min.) and an oxygen gas (206 ml/min.) were respectively supplied under atmospheric pressure (in terms of 0 °C, 1 atm). The quartz reaction tube was heated in an electric furnace to adjust the internal temperature (hot spot) to 300°C. 1.8 Hours after the beginning of the reaction, the gas at the reaction outlet was sampled by passing it through an aqueous 30 wt% potassium iodide solution, and then the amount of chlorine formed and amount of the non-reacted hydrogen chloride were respectively determined by iodometric titration and neutralization titration .

The formation activity of chlorine per unit weight of the catalyst determined by the following equation was  $5.1 \times 10^{-4}$  mol/min.g-catalyst.

Chlorine formation activity per unit weight of catalyst  
(mol/min.g-catalyst) = amount of outlet chlorine formed  
(mol/min)/weight of catalyst (g)

The formation activity of chlorine per unit weight of Ru determined by the following equation was  $346 \times 10^{-4}$  mol/min.g-Ru.

Chlorine formation activity per unit weight of Ru (mol/min.g-

Ru) = amount of outlet chlorine formed ( mol/min)/weight of Ru (g)

#### Sample B

A catalyst was prepared by the following process. That is, 60g of a titanium oxide powder (P25, manufactured by Nippon AEROSIL Co., Ltd. rutile crystal was 17%) was kneaded with 36.0 g of pure water, 3.0g of Metholose (methyl cellulose, 65SH-4000, manufactured by Shinetsu Chemical Co., Ltd.) and 7.89 g of a titanium oxide sol (CSB, TiO<sub>2</sub> content: 38% by weight, manufactured by Sakai Chemical Industry Co., Ltd.). The mixture was sufficiently kneaded. This kneaded one was extruded into a form of a noodle of 1.5 mm  $\phi$  in size. After drying under air at 60°C for 4 hours, a white noodle-shaped titanium oxide was obtained. After heating under air from room temperature to 600°C over 1.75 hours, calcination was conducted at the same temperature for 3 hours. After the completion of the calcination, 56.3 g of a white extruded titanium oxide was obtained by cutting the noodle-shaped solid into pieces of about 5 mm in size. Then, 50.0 g of the resulting carrier was impregnated with an aqueous solution prepared by dissolving 2.03 g of commercially available ruthenium chloride (RuCl<sub>3</sub>·nH<sub>2</sub>O, Ru content: 37.3% by weight) in 15.0 g of pure water, and dried at 60°C for 4 hours to obtain 51.9 g of a ruthenium chloride supported on titanium oxide. Then, 25.9g of resulting solid was dipped in a mixture of 10.5 g of a 2N potassium hydroxide solution and 50 g of pure water, and then in a mixture of 2.54 g of hydrazine monohydrate and 25 g of pure water under nitrogen at room temperature, followed by dipping for 1 hour with stirring every 15 minutes after the reduction, filtration was conducted by using a glass filter. Bubbling occurred on dipping. 500 ml of pure water was added, followed by washing for 30 minutes and further separation by filtration. This operation was repeated five times. The pH of the wash was 10.3 at the first time, and the pH of the wash was 8.35 at the fifth time. To the resulting extruded solid separated by filtration, 125 g of a 0.5 mol/l of potassium chloride solution was added and, after stirring and allowing to stand 30 minutes, the resulting extruded solid was separated by filtration again. This operation was repeated three times. The resulting extruded solid was dried at 60°C for 4 hours to obtain a gray solid. After heating from

room temperature to 350°C under air over 1 hour, the solid was calcined at the same temperature for 3 hours. After the completion of the calcination, 500 ml of pure water was added and the mixture was stirred and, furthermore, the solid was separated by filtration. This operation was repeated five times over 5 hours and, after adding dropwise an aqueous silver nitrate solution to the wash, it was confirmed that potassium chloride is not remained. Then, 25.3 g of a bluish gray extruded ruthenium oxide catalyst supported on titanium oxide was obtained by drying this resultant extruded solid at 60°C for 4 hours.

Incidentally, the calculated value of the content of ruthenium oxide was as follows.

$$\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2(17\% \text{ rutil crystal}) + \text{TiO}_2(\text{binder})) \times 100 = 2.0\%$$

by weight

The calculated value of the content of ruthenium was as follows.

$$\text{Ru} / (\text{RuO}_2 + \text{TiO}_2(17\% \text{ rutil crystal}) + \text{TiO}_2(\text{binder})) \times 100 = 1.5\%$$

by weight

The ruthenium oxide catalyst supported on titanium oxide (2.5 g) thus obtained was charged in a quartz reaction tube (inner diameter: 12 mm) in the same manner as that described in Sample A, and then the reaction was conducted according to the same reaction manner as that described in Sample A except that the hydrogen chloride (211ml/min) and the oxygen gas (211ml/min) were passed through the reaction tube. 1.8 Hours after the beginning of the reaction, the formation activity of chlorine per unit weight of the catalyst was  $6.2 \times 10^{-4}$  mol/min.g-catalyst.

The formation activity of chlorine per unit weight of the Ru was  $418 \times 10^{-4}$  mol/min.g-Ru.

#### Sample C

A catalyst was prepared by the following process. A solution of commercially available ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 wt %) (3.24 g) and pure water (20.6 g) was hydrolyzed by a mixture of 85wt% potassium hydroxide solution (2.39 g) and pure water (17.8 g). To this mixture, a commercially available  $\alpha$ -alumina (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (60 g) and alumina sol (ALUMINA SOL 200 manufactured by Nissan Chemical Industries, Ltd.,

Al<sub>2</sub>O<sub>3</sub> content is 10.4 wt%) (17.23 g) were added and thoroughly mixed. The mixture was sufficiently kneaded until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm  $\phi$ , and dried under air at 60°C for 4 hours to obtain gray noodle-form ruthenium oxide-  $\alpha$ -alumina.

The obtained gray noodle-form ruthenium oxide-  $\alpha$ -alumina was heated under an air stream from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours. After the completion of the calcination, 500 ml of pure water was added and the mixture was stirred and, furthermore, the solid was separated by filtration. This operation was repeated five times over 5 hours and, after adding dropwise an aqueous silver nitrate solution to the wash, it was confirmed that potassium chloride is not remained. Then, gray noodle-form ruthenium oxide catalyst supported on  $\alpha$ -alumina was obtained (48.7 g).

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2 / (\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 2.55 \text{ wt } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru} / (\text{RuO}_2 + \alpha\text{-Al}_2\text{O}_3)] \times 100 = 1.95 \text{ wt } \%$$

The ruthenium oxide catalyst supported on  $\alpha$ -alumina (2.5 g) thus obtained was charged in a quartz reaction tube (inner diameter: 12 mm) in the same manner as that described in Sample A, and then the reaction was conducted according to the same reaction manner as that described in Sample A except that the hydrogen chloride (210ml/min) and the oxygen gas (210ml/min) were passed through the reaction tube and the internal temperature was adjusted to 301°C. 2.0 Hours after the beginning of the reaction, the formation activity of chlorine per unit weight of the catalyst was  $1.75 \times 10^{-4}$  mol/min.g-catalyst.

#### Sample D

A catalyst was prepared by the following process. A commercially available  $\alpha$ -alumina (AES-12 manufactured by Sumitomo Chemical Co., Ltd.) (400 g), ruthenium chloride ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , ruthenium content: 37.3 wt %) (53.66 g), pure water (1.91 g) and alumina sol (ALUMINA SOL 200 manufactured by Nissan Chemical Industries, Ltd., Al<sub>2</sub>O<sub>3</sub> content is 10.4 wt%) (192.3 g) were thoroughly mixed. The mixture was sufficiently

kneaded until an adequate viscosity was reached.

This mixture was molded by extrusion in the form of noodles having a diameter of 1.5 mm  $\phi$ , and dried under air at 60°C for 4 hours to obtain brown noodle-form ruthenium chloride-  $\alpha$ -alumina.

The obtained brown noodle-form ruthenium chloride- $\alpha$ -alumina was heated under air stream from room temperature to 350°C over 1 hour and calcined at the same temperature for 3 hours to obtain gray noodle-form ruthenium oxide catalyst supported on  $\alpha$ -alumina.

The calculated content of ruthenium oxide was as follows:

$$[\text{RuO}_2/(\text{RuO}_2+\alpha\text{-Al}_2\text{O}_3)] \times 100 = 5.9 \text{ wt } \%$$

The calculated content of ruthenium was as follows:

$$[\text{Ru}/(\text{RuO}_2+\alpha\text{-Al}_2\text{O}_3)] \times 100 = 4.5 \text{ wt } \%$$

The ruthenium oxide catalyst supported on  $\alpha$ -alumina (2.5 g) thus obtained was charged in a quartz reaction tube (inner diameter: 12 mm) in the same manner as that described in Sample A, and then the reaction was conducted according to the same reaction manner as that described in Sample A except that the oxygen gas (184ml/min) were passed through the reaction tube and the internal temperature was adjusted to 301°C. 1.8 Hours after the beginning of the reaction, the formation activity of chlorine per unit weight of the catalyst was  $2.27 \times 10^{-4}$  mol/min.g-catalyst.

#### Life Test of the Catalysts

In this step, the Catalysts sample A and Sample C were used in Experimental 1, and Sample B and Sample D were used in Experimental 2.

##### Experimental 1.

In a nickel test reactor tube having an inner diameter of 14 mm, in which a thermocouple-protective tube having an outer diameter of 5 mm was inserted, Catalysts sample C and sample A were charged in a volume ratio of 1.7:15.7 (C:A) from the inlet of a reactor. Each Catalyst had been diluted with the same volume ratio of  $\alpha$ -alumina spheres having a diameter of 2 mm (SSA 995 manufactured by NIKKATO). The charged volumes of Sample C and A were as follows:

Sample C: 1.7 ml (1.84 g)

Sample A: 15.7 ml (12.9 g)

The total volume of charged catalysts was 17.4 ml.

The zone of the Catalyst layer was formed by the Sample C and the Sample A and the zone was heated in an electric furnace.

Hydrogen chloride gas and oxygen gas were supplied and flowed under atmospheric pressure from the upper inlet to the down outlet at flow rates of 130 ml/min. and 65 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.) This reaction operation was carried out for 593 hours under the same conditions while maintaining the conversion of hydrogen chloride at higher than 70 %. After 593 hours, the internal temperature (hot spot) of the catalysts zone in the test reactor tube was 368°C. At this time, the conversion of hydrogen chloride was 84.9 %.

Furthermore, the activity of Sample A was measured as follows:

Sample A was isolated from the mixture of Sample A and the  $\alpha$ -alumina carrier used in the above step, and 2.5 grams of Sample A was thoroughly mixed again with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (10 g) to dilute Sample A, and diluted Sample A was charged in a quartz reactor tube having an inner diameter of 12 mm. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. and 192 ml/min., respectively. The quartz reactor tube was heated with an electric furnace to keep the internal temperature (hot spot) at 300°C. When 1.8 hours after the start of the reaction, the chlorine formation activity per unit weight of the catalyst was  $2.96 \times 10^{-4}$  mol/min.g-cat.

## Experimental 2.

In a nickel test reactor tube having an inner diameter of 14 mm, in which a thermocouple-protective tube having an outer diameter of 5 mm was inserted, Catalysts sample D and sample B were charged in a volume ratio of 2.5:15.0 (D:B) from the inlet of a reactor. Each Catalyst had been diluted with the same volume ratio of  $\alpha$ -alumina spheres having a diameter of 2 mm (SSA 995 manufactured by NIKKATO). The charged



volumes of Sample D and B were as follows:

Sample D: 2.5 ml (3.14 g)

Sample B: 15.0 ml (14.4 g)

The total volume of charged catalysts was 17.5 ml.

The zone of the Catalyst layer was formed by the Sample D and the Sample B and the zone was heated in an electric furnace.

Hydrogen chloride gas and oxygen gas were supplied and flowed under atmospheric pressure from the upper inlet to the down outlet at flow rates of 131 ml/min. and 67 ml/min., respectively (each converted to a volume at 0°C under 101 kPa.) This reaction operation was carried out for 307 hours under the same conditions while maintaining the conversion of hydrogen chloride at higher than 55 %. After 307 hours, the internal temperature (hot spot) of the catalysts zone in the test reactor tube was 348°C. At this time, the conversion of hydrogen chloride was 76.8 %.

Furthermore, the activity of Sample B was measured as follows:

Sample B was isolated from the mixture of Sample B and the  $\alpha$ -alumina carrier used in the above step, and 2.5 grams of Sample B was thoroughly mixed again with the commercially available spherical  $\alpha$ -alumina carrier having a diameter of 2 mm (SSA 995 manufactured by NIKKATO) (10 g) to dilute Sample B, and diluted Sample B was charged in a quartz reactor tube having an inner diameter of 12 mm. Then, hydrogen chloride gas and oxygen gas were supplied in the quartz reactor tube under atmospheric pressure at flow rates of 192 ml/min. and 184 ml/min., respectively. The quartz reactor tube was heated with an electric furnace to keep the internal temperature (hot spot) at 300°C. When 2.0 hours after the start of the reaction, the chlorine formation activity per unit mass of the catalyst was  $2.29 \times 10^{-4}$  mol/min.g-cat.

Table 1 Catalytic Activity in Oxidation Reaction of Hydrogen Chloride

Sample	Catalyst	Kind of TiO <sub>2</sub>	Catalytic Activity* after 2hr Reaction (E)	Catalytic Activity* after Reaction Finished (F)	F/E
A	2wt%RuO <sub>2</sub> /TiO <sub>2</sub>	STR-60R(rutile content:100%)	5.1	2.96(after 593hr)	0.59
B	2wt%RuO <sub>2</sub> /TiO <sub>2</sub>	P25(rutile content:20%)	6.2	2.29(after 307hr)	0.37

\* :  $\times 10^{-4} \text{Cl}_2 \cdot \text{mol} \cdot \text{min}^{-1} \cdot \text{gcat}^{-1}$

### Experimental 3.

The sample E was prepared by the following process. That is, 50.0 g of a titanium oxide powder (STR-60N, 100% rutile crystal, manufactured by Sakai Chemical Industry Co., Ltd.) was kneaded with 33.4 g of pure water and 6.6 g of a titanium oxide sol (CSB, TiO<sub>2</sub> content: 38% by weight, manufactured by Sakai Chemical Industry Co., Ltd.). At room temperature, a dry air was blown to the kneaded one, which was then dried until suitable viscosity was obtained. The weight loss of water by drying was 0.2 g. After drying, the mixture was sufficiently kneaded again. The kneaded one was extruded into a form of a noodle of 1.5 mm  $\phi$  in size. After drying under air at 60°C for 4 hours, 46.3 g of a white noodle-shaped titanium oxide was obtained. After heating under air from room temperature to 500 °C over 1.3 hours, calcination was conducted at the same temperature for 3 hours. After the completion of the calcination, 45.3 g of a white extruded titanium oxide carrier was obtained by cutting the noodle-shaped solid into pieces of about 5 mm in size. Then, 40.0 g of this carrier was impregnated with an aqueous solution prepared by dissolving 3.23 g of commercially available ruthenium chloride (RuCl<sub>3</sub>·nH<sub>2</sub>O, Ru content: 37.3% by weight) in 21.9 g of pure water, and dried at 60°C for 2 hours. Then, the resulting

solid was dipped in a solution of 16.7 g of a 2N potassium hydroxide solution, 241 g of pure water and 4.1 g of hydrazine monohydrate under nitrogen at room temperature, with stirring every 15 minutes. Bubbling occurred on dipping. After 80 minutes, filtration was conducted by using a glass filter. Washing was conducted for 30 minutes by adding 500 ml of water, followed by filtration. This operation was repeated five times. The pH of the wash was 9.2 at the first time, and the pH of the wash was 7.2 at the fifth time. To the extruded solid separated by filtration, 50 g of a 0.5 mol/l of potassium chloride solution was added and, after stirring, the extruded solid was separated by filtration again. This operation was repeated three times. The resulting solid was dried at 60°C for 4 hours to obtain a gray solid. After heating from room temperature to 350°C in an air over 1 hour, the solid was calcined at the same temperature for 3 hours. After the completion of the calcination, 500 ml of pure water was added and the mixture was stirred and, furthermore, the solid was separated by filtration. This operation was repeated ten times and, after adding dropwise an aqueous silver nitrate solution to the wash, it was confirmed that potassium chloride is not remained. Then, 41.1 g of a bluish gray extruded ruthenium oxide catalyst supported on titanium oxide was obtained by drying this solid at 60°C for 4 hours.

Incidentally, the calculated value of the content of ruthenium oxide was as follows.

$$\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2) \times 100 = 3.8\% \text{ by weight}$$

The calculated value of the content of ruthenium was as follows.

$$\text{Ru} / (\text{RuO}_2 + \text{TiO}_2) \times 100 = 2.9\% \text{ by weight}$$

X-ray diffraction analysis of the titanium oxide powder (STR-60N) used was conducted under the same conditions as those of Example 1. As a result, a peak intensity of a rutile crystal ( $2\theta = 27.4^\circ$ ) was 1015 cps. On the contrary a anatase crystal ( $2\theta = 25.3^\circ$ ) peak was not detected. Consequently, the content of the rutile crystal was 100%.

According to the same reaction manner as that described in Example 2 except that the catalyst was diluted by mixing 2.50 g of the ruthenium oxide catalyst supported on titanium oxide thus obtained with 10 g of a commercially available spherical (2 mm in size) alumina carrier (SSA995, manufactured by Nikkato Co.) and then charged in a quartz

reaction tube (inner diameter: 12 mm) and that the oxygen gas (192 ml/min.) was passed through the reaction tube and the internal temperature was adjusted to 298 °C, the reaction was conducted. 2.3 Hours after the beginning of the reaction, the formation activity of chlorine per unit weight of the catalyst was  $8.88 \times 10^{-4}$  mol/min.g-catalyst.

#### Experimental 4.

The sample F was prepared by the following process according to J. Electrochem. Soc., 1034, 140, (1993) which illustrates prepared RuO<sub>2</sub>-TiO<sub>2</sub> showing a single crystal. That is, a commercially available ruthenium chloride (RuCl<sub>3</sub>.nH<sub>2</sub>O Ru content: 38.2 wt%) and Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> were used as the starting materials. The RuCl<sub>3</sub>.nH<sub>2</sub>O was dried at 160 °C for 3 h under reduced pressure. A required amount (1.039g) of the dehydrated ruthenium chloride was dissolved in 500 ml of anhydrous ethanol, and the stoichiometric quantity (three times mol of ruthenium) of an anhydrous ethanol solution (100 ml) of sodium ethylate (1.02g) was added to it. Ruthenium alkoxide was synthesized by refluxing of the solution at 78 °C for 3 h under dried nitrogen atmosphere. When the resulting solution was cooled to room temperature. 15.7g of Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> was added to it, and this solution was stirred for 5 min. A solution containing the metals Ru and Ti was prepared in this experiment. The mixture of ruthenium and titanium alkoxides was hydrolyzed by adding 455 ml of ammonia-ethanol solution (50 mmol NH<sub>3</sub> in 1 L ethanol) was stirring. After stirring for 5 min, 100 ml of 30 % H<sub>2</sub>O<sub>2</sub> was slowly added to it. The hydrolysis product was separated by filtration, washed three times in 100 ml of 3% H<sub>2</sub>O<sub>2</sub>, and then put in a porcelain tray followed by drying in an oven at 90 °C for 10 h. And then the solid was calcined at 250 °C 3 h, 450 °C 3 h. 2.75 g of mixed oxide of RuO<sub>2</sub>-TiO<sub>2</sub> was prepared.

Incidentally, the calculated value of the content of ruthenium oxide was as follows.

$$\text{RuO}_2 / (\text{RuO}_2 + \text{TiO}_2) \times 100 = 10.8\% \text{ by weight}$$

X-ray diffraction analysis of the product powder was conducted. The crystal structure of the powder was rutile crystal.

The product powder (2g) was mixed with AEROSIL silica powder (2g) sufficiently, and pressed to mold, next crashed to granulate to a

catalyst of 1mm to 2mm.

The ruthenium oxide-titanium oxide, mixed oxide catalyst (2.5 g) thus obtained was charged in a quartz reaction tube (inner diameter: 12 mm) in the same manner as that described in Sample A, and then the reaction was conducted according to the same reaction manner as that described in Sample A except that the hydrogen chloride (192ml/min) and the oxygen gas (192ml/min) were passed through the reaction tube. 1.8 Hours after the beginning of the reaction, the formation activity of chlorine per unit weight of the catalyst was  $0.73 \times 10^{-4}$  mol/min.g-catalyst.

Table 2 Catalytic Activity in Oxidation Reaction of Hydrogen Chloride

Sample	Catalyst	Kind	Catalytic Activity* after 2hr Reaction
E	3.8wt%RuO <sub>2</sub> /TiO <sub>2</sub>	supported catalyst	8.88
F	5.4wt%RuO <sub>2</sub> -TiO <sub>2</sub> /SiO <sub>2</sub>	mixed oxide catalyst	0.73

\* :  $\times 10^{-4}$  Cl<sub>2</sub>-mol·min<sup>-1</sup>·gcat<sup>-1</sup>

That I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above identified application or patent issued thereon.

Date: October 26, 2000 — Kohei Seki  
Kohei SEKI